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Project Summary

Evaluation of Methods for Collecting Dislodgeable Pesticide Residues from Turf

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Three surface dislodgeable residue collection methods were evaluated in two tests performed on turf treated with pesticide formulations. The test plots used were typical of the turf found in lawns of local residents. The polyurethane foam (PUF) roller and the Dow sled methods were tested side-by-side on turf treated with a mixture of chlorpyrifos and chlorothalonil. The PUF roller and California roller methods were tested side-by-side on turf treated with a mixture of dicamba, mecoprop, and 2,4-D. A pressurized tank sprayer was used to apply the pesticide formulations according to manufacturer's label directions. Test plots were mowed so that the mower direction was kept the same over the entire plot. Both tests were conducted by performing replicate sampling in separate areas of the plots so that the sampler direction was with, against, or across the cutting direction of the mower.

All three test methods were evaluated on the basis of their sampling precision and transfer efficiency data. Another important criterion considered was the affinity of the sample media to become contaminated with grass clippings and debris during sample collection. Low recoveries of target analytes from some spiked media samples were an additional consideration. After considering all of these factors, we determined that the PUF roller method was the least suitable for turf residue sampling under our test conditions. The Dow sled method was more suitable, but the small sled proved unstable in tests on deeper turf, so the test data was limited. The California roller method proved to be the most suitable procedure.

This Project Summary was developed by the National Exposure Research Laboratory's Human Exposure and Atmospheric Sciences Division, Research Triangle Park, NC, to announce key findings of the evaluation that is fully documented in a separate report (see ordering information at back.)

Introduction

The levels and distribution of pesticide residues in residential environments is a subject of concern because of the potential exposure risk such contaminants pose for small children. The application of pesticides to residential lawns for control of insects, weeds, and turf diseases constitutes the primary source of surface dislodgeable residues. The U.S. Environmental Protection Agency has been active in conducting research efforts to develop methodologies for monitoring surface dislodgeable pesticide residues on indoor surfaces and floors and on outdoor surfaces and lawns. These efforts are in response to the Office of Pollution Prevention and Toxics, which is currently involved in the development of testing guidelines for post-application exposure. The guidelines are applicable to both occupational reentry and residential exposure and are designed to cover data requirements necessary to support the registration of pesticide products under 40 CFR part 158.

A recent study designed to measure the transport of lawn-applied acid herbicides from turf into the home used human subjects to simulate track-in transport of dislodgeable residues from treated turf plots to outside doormats and indoor carpet surfaces. The Southwest Research Institute (SwRI) PUF roller method was used to monitor dislodgeable residues on both the indoor carpet surfaces and on the treated turf plot. A round-robin test was just recently conducted to evaluate the PUF roller and two other methods in measuring dislodgeable pesticide residues on indoor carpet. In this current study, those same three methods, the SwRI PUF roller, the California cloth roller, and the Dow drag sled were evaluated in two tests conducted on treated turf.

The turf test plots used in this study were located on the grounds of a ManTech Environmental facility in Research Triangle Park, NC. While the grounds are maintained by a professional service, the test plots used here were not of the high quality that would be found at a turf research facility. Consequently, they were more typical of the "real world" residential lawn in that they contained a substantial portion of weeds and exhibited a more uneven and generally lower turf density. After mowing, two separate test plots were treated with commonly used formulations: an insecticide and fungicide in the first test, and an acid herbicide mixture in the second test. Deposition coupons were placed on the test surface prior to spraying the formulations to determine the amount and uniformity of the pesticide application. Field blank samples and field spike samples were collected for each method used in each test. Written standard operating procedures (SOPs) for the test methods were followed in performing replicate sampling on each test plot.

The test results were used to calculate the sampling precision for each target analyte in terms of the percent relative standard deviation of three replicate samples for each method. The transfer efficiency of each method was determined by calculating the ratio of the average transfer rate to the average deposition rate for each target analyte as determined by analysis of the deposition coupon samples. The performance of each dislodgeable residue sampling method was evaluated based on these results and on other key factors relating to the sample media, sample handling, and the quality control sample analysis results. All of the analytical laboratory work performed in this study was provided by Southwest Research Institute, San Antonio, TX. In addition to performing all of the test sample extraction and GC/MS analysis work, they provided all of the pre-cleaned sample media and the laboratory standard spike solutions.

Study Design

Turf test plots were designed to contain three separate 8- x 10-ft sections that would permit the collection of three replicate samples with each test method in each section. The plots were mowed one day prior to the test application and in a manner such that the mower direction was kept constant throughout the process. Sampling was then performed so that the sampler direction in each test section varied relative to the cutting direction of the mower, that is, the same direction, the perpendicular direction, and the opposite direction.

Combination Insecticide and Fungicide Application Test

This test was designed to evaluate the PUF roller method and the Dow drag sled method in side-by-side sampling. The sample traverse for both methods was a single pass of 2.0 m in length. A commercially available mixture of the insecticide chlorpyrifos and the fungicide chlorothalonil was prepared in water and applied according to manufacturer's recommendations. The formulation (0.17% chlorpyrifos, 1.41% chlorothalonil) was applied at a rate of 1 gal/500 ft^2 using a compressed air tank sprayer. Three α-cellulose deposition coupons were evenly distributed over each test section prior to spraying. This test was conducted in hot and relatively dry conditions during the month of July.

Acid Herbicide Application Test

This test was designed to evaluate all three of the dislodgeable residue test methods, including the California roller method. The procedures employed in the first test were generally followed. Due to the additional sampling area required by the addition of the California roller method to the test protocol, a fourth test section was prepared for treatment. Two replicate samples were collected with the California roller method in each of the first three test sections, and an additional three samples were collected in the fourth section. A commercial mixture of acid herbicides was mixed in water according to manufacturer's recommendations yielding a formulation containing 0.007% dicamba, 0.03% mecoprop, and 0.06% 2,4-D. The mixture was applied to the test plot at a rate of 1 gal/250 ft^2. In contrast to the conditions that marked the first test in this study, this second test was conducted during cool and relatively wet conditions in the month of October.

Test Methods

α-Cellulose Deposition Coupon

The deposition coupons used were 100-mm squares of cellulose filter paper attached to aluminum foil-covered backing sheets of the same size. Each coupon was marked by pencil line so that a 12.5-mm (0.5-in.) border on all sides was available to allow handling. Prior to extraction, the coupon border was trimmed away to leave a 75-mm square (56.25 cm^2) filter sample for analysis in the laboratory. Estimates of the deposition rate for a given sample were determined from the ratio of the mass of pesticide residue found on the coupon to its area and were usually reported in units of micrograms per square centimeter.

PUF Roller

The PUF roller dislodgeable residue sampling method uses a prototype mechanical apparatus having two rear wheels, a cylindrical aluminum roller at the front, and a handle for pushing or pulling attached at the rear. Two stainless steel blocks (total weight = 3.97 kg) are attached to the center portion of the frame. A PUF ring measuring 90-mm o.d.- x 30-mm i.d.- x 76-mm in length was fitted onto the aluminum cylinder, which was then attached to the front of the sampler assembly.

The location of the sample was marked on the test plot by placing a metal guidebar adjacent to the planned track of the device. The 200-cm sample traverse distance was marked off in 10-cm segments on the bar. A solvent-washed thin aluminum sheet was placed at the starting position to serve as a platform to hold the PUF roller before starting the test.

A sample traverse consisted of a single pass over the 200-cm pathlength. At the end of the traverse, the roller was immediately lifted off of the turf. The aluminum cylinder was then detached from the assembly, and the PUF ring was recovered and stored in its container. The marks at 10-cm intervals on the guidebar were used to assist the operator in maintaining the sampling rate at about 10 cm/s.

Dow Drag Sled

The Dow drag sled procedure uses a 3- x 3-in. piece of 3/4-in.-thick plywood as the base for a sled with a ridge constructed on the top to hold an 8-lb round downrigger weight. A screw eye is placed in the center of one edge of the block, to which a 24-in long wire and pull handle are attached. The base and sides of the sled are covered with two layers of aluminum foil attached with staples.

The sampling media consists of precleaned 4- x 4-in. undyed cotton denim cloth squares. A thin aluminum sheet starting platform and a metal guidebar were used with the Dow sled procedure. A sample traverse consisted of a single pass with the sled over a distance of 200 cm using guide marks at 10-cm intervals to achieve an approximate sampling rate of 10 cm/s.

The denim cloth sampling media is attached to the base of the sled by using plastic-headed pushpins positioned through the overlapping edges of the cloth and into the front and sides of the wooden sled. With the denim cloth securely in place, the sled was placed on the aluminum starting platform, and the 8-lb weight was put into its position on top of the sled. The drag line was then attached to the screw eye on the front of the sled. Keeping the drag line at a low angle relative to the ground, the operator pulled the sled forward at a steady rate until the front of the sled reached the 200-cm mark on the guidebar. The sled was then quickly lifted from the turf, and the denim cloth was removed from the sled, then folded and stored in its container.

California Roller

The California roller method uses a device resembling a large rolling pin to collect surface dislodgeable residues on a percale sheet cloth matrix. The roller consists of a 63-cm-long PVC pipe, 13 cm in diameter, that is fitted with PVC endcaps having roller handles. The roller is covered with a 1-cm-thick foam cover, 51 cm in length, and is filled with a quantity of small to medium-size steel ball bearings sufficient to bring the total weight of the roller to 11.3 kg.

The sampling medium, consisting of a precleaned 17- x 17-in. cloth cut from percale bedsheet material (50% combed cotton, 50% Fortrel® polyester, 180 thread count), is placed flat on the turf and covered with a plastic sheet (e.g. medium-size plastic trash bag, 20- x 24-in.). The plastic sheet is held in place by driving 6-in.-long metal spikes through the corners of the sheet and into the ground. Sampling is performed by moving the roller back and forth ten times at a steady rate over the sample medium (20 total passes). A special metal handle assembly was fabricated for use in these tests to permit the operator to more comfortably move the roller without exerting any downward pressure on the handles. After the final sample pass, the roller and handle assembly are removed from the test area, the metal spikes are removed, and the plastic sheet is discarded. Forceps are then used to collect and fold the percale cloth for insertion into its sample container.

Sample Analysis

A wide variety of samples were handled and analyzed in this study. In addition to the three types of dislodgeable residue samples collected from the two differently treated test plots, quality control samples were collected that included field blanks, field spikes, raw formula samples, and grass clippings and debris removed from test sample media. The analytical laboratory, SwRI, followed specific SOPs for extraction and analysis of each sample type and group of target analytes to be determined. The laboratory also performed its own internal quality control procedures that included analysis of media and solvent blanks, spiked samples, and addition of surrogate compounds before extraction to test sample recovery levels. Sample extraction procedures for the chlorpyrifos/chlorothalonil samples involved a cold-shake extraction in solvent, concentration by evaporation, and Florisil cleanup. Sample extracts were then analyzed by GC/MS using the selected ion monitoring mode. Acid herbicide samples were extracted in an acidified water/ethanol solution followed by liquid-liquid extraction with chloroform, solvent exchange, and then derivatization to the methyl ester form of the compounds. Analysis was by GC/MS using a Fisons VG-MD800 instrument.

Results and Discussion

Analytical results for field and laboratory blanks and GC/MS calibrations were acceptable in all cases. Surrogate compound recoveries were acceptable for all samples with two exceptions that were so noted. Analysis of field and laboratory spiked samples for chlorpyrifos and chlorothalonil were acceptable for all media except for low recoveries (68%) of chlorothalonil on the PUF media. Analysis of field and laboratory spiked samples for dicamba, mecoprop, and 2,4-D yielded generally poor results. Only the percale sheet (California roller method) media yielded acceptable recoveries of all three target analytes averaging 84% recovery, with a minimum of 76%. The results indicate inefficient extraction of the target analytes from the PUF media and the denim cloth media. Recoveries ranged from a high of 69% for dicamba to a low of 34% for 2,4-D, both from the PUF media.

Combination Insecticide and Fungicide Application Test

The turf plot used in this test was mowed to a height of two inches, and a four hour drying period was allowed following application of the pesticide formulation. The deposition rate and uniformity of the application were determined by placing three deposition coupons in each of the three test plot sections before spraying the turf plot. The centrally located coupon in each section was recovered immediately after the spraying was completed. The remaining coupons were recovered at intervals concurrent with the individual sampling operations. In each test section the two remaining coupons were combined for analysis as a single sample. A uniform application was indicated based on the results for both sets of deposition coupons. The calculated average deposition rate and the corresponding percent relative standard deviation for chlorpyrifos for coupons collected immediately were 14.7 $\mu g/cm^2 \pm$ 10.9%, and for those collected later in the day the results were 2.64 $\mu g/cm^2 \pm$ 9.4%. The corresponding data for chlorothalonil was 180.6 $\mu g/cm^2 \pm$ 11.2% and 139.2 $\mu g/cm^2 \pm$ 3.7%. The large decrease in the levels of chlorpyrifos during the drying period attests to the high volatility of this compound.

The overall results for this test are presented in Table 1 for both the PUF roller and the Dow drag sled methods. The method transfer rate is the ratio of the total pesticide collected to the total area covered during the sample traverse. The sampling precision is the calculated percent relative standard deviation for replicate sample results. The method transfer efficiency is the ratio of the method transfer rate to the pesticide deposition rate as determined by the combined analysis of the two depositions collected from each test plot section at the time of sampling.

The sampling precision results were mixed and not particularly good for either of the two methods evaluated in this test. The average transfer rate and the corresponding transfer efficiency of the PUF roller method were approximately twice that of the Dow drag sled method for both target compounds used.

Acid Herbicide Application Test

The turf plot used for this test was mowed to a height of three inches, and a three hour drying period was allowed following application of the acid herbicide formulation. The deposition rate and uniformity of the pesticide application were determined for this test by using deposition coupons in the same way as in the earlier test. The calculated average deposition rate and the corresponding percent relative standard deviation for dicamba for coupons collected immediately were 0.36 $\mu g/cm^2 \pm$ 4.7%, and for those collected later in the day the results were 0.36 $\mu g/cm^2 \pm$ 10.0%. The corresponding data for mecoprop was 1.12 $\mu g/cm^2 \pm$ 5.6% and 0.96 $\mu g/cm^2 \pm$ 17.2%. And for 2,4-D the results were 2.64 $\mu g/cm^2 \pm$ 14.0% and 2.82 $\mu g/cm^2 \pm$ 12.9%. These results show that the application was uniform, and that the levels of all three target compounds remained stable throughout the drying period.

Table 1. Combination Insecticide and Fungicide Test Results

Method & Target Compounds	Transfer Rate (mg/cm^2)	Sampling Precision	Transfer Efficiency
PUF Roller			
Chlorpyrifos	2.37	30.8%	0.087%
Chlorothalonil	401	62.0%	0.293%
Dow Drag Sled			
Chlorpyrifos	1.05	50.3%	0.0390%
Chlorothalonil	240	19.3%	0.173%

At the onset of the sampling activities for this test a problem was encountered with the Dow drag sled procedure. The weighted sled could not be dragged over the turf surface without it falling over numerous times during a 200-cm traverse. It appears that the small sled, while functioning normally in tests on shorter turf (two inches high) earlier, could not remain stable in the longer turf used for this test. Consequently, the Dow drag sled was not included in the sampling schedule conducted on this test plot. Other studies have been conducted using larger drag sleds that have been found to be stable for turf applications, but such a sled was not available for use in this test. The overall results are presented in Table 2 for both the PUF roller and California roller methods. The method parameters shown are the same as reported for the combination insecticide and fungicide earlier.

The results of the acid herbicide application test are definitive. The sampling precision and transfer efficiency of the PUF roller method were similar to those same results from the first test performed. In both cases the method exhibited relatively low precision and variable transfer efficiency results. In contrast, the California roller method exhibited relatively high precision and consistent transfer efficiency results for this one test in which it was evaluated.

Analysis of Grass Clippings and Debris Removed from Sample Media

A problem developed early on in this study involving the grass clippings and other debris that adhered to the sample media following the performance of the dislodgeable residue test runs. The problem was particularly serious for the PUF roller sample media. Both the drag sled denim cloth media and the California roller percale sheet media were found to collect small amounts of clippings and debris, but these could be easily removed by the laboratory analyst. The PUF roller media, on the other hand, collected much larger quantities of the debris, and it adhered more strongly making removal tediously difficult. Prior to extraction and analysis of every sample collected during this study, the sample media were meticulously cleaned of debris and the removed material was saved for later gravimetric and chemical analysis. Analysis of debris material removed from two each of the PUF roller and Dow sled samples from the first test revealed that the impact of the grass and debris adhering to the media following sampling was significant in the case of the PUF roller for chlorpyrifos. Because of the relatively low chlorpyrifos concentrations and the greater bulk of grass and debris collected on the PUF media versus the Dow denim cloth, more than 25% of the total chlorpyrifos collected by the PUF roller was due to grass and debris, while less than 10% of the Dow sled chlorpyrifos was due to extraneous material. The much higher sample concentrations of chlorothalonil significantly reduced the impact of grass and debris contributions to the sample totals for both methods, although the PUF roller samples averaged about 5% of the total collected, while the Dow sled samples were below analytical detection limits. Three samples each of the debris removed from the PUF roller media and the California roller media used in sampling for the acid herbicide test were similarly analyzed. The calculations showing the percentage contribution of the media sample and the debris sample to the total sample results revealed the significance of the problem posed by extraneous material picked up by sample media during tests on turf. For the PUF roller test runs, more than 97% of the total analyte concentration for all three acid herbicide constituents was in the grass clippings and debris sample fraction. And even though the amount of grass and debris removed from the percale sheet media was much less than that from the PUF sleeve, the grass clipping and debris sample fraction accounted for about 70% of the total analyte concentration for all three acid herbicide constituents in those samples. Gravimetric analysis of the extraneous material removed from all three types of sample media used in these tests showed that the PUF roller media collected an average of 17.4 mg of debris. The average amount removed from California roller percale sheet media was 6.4% of that amount, and debris removed from the Dow sled denim cloth media was only 1.5% of the PUF roller amount. These results should serve to emphasize the need to ensure that sampling media used in turf measurements for pesticide residues be scrupulously cleaned of any and all extraneous material prior to extraction and analysis.

Table 2. Acid Herbicide Test Results

Method & Target Compounds	Transfer Rate (mg/cm^2)	Sampling Precision	Transfer Efficiency
PUF Roller			
Dicamba	0.66	43.7%	0.184%
Mecoprop	2.48	46.2%	0.257%
2,4-D	4.89	47.7%	0.171%
California Roller			
Dicamba	1.78	12.2%	0.504%
Mecoprop	5.19	13.1%	0.548%
2,4-D	15.63	10.1%	0.560%

Conclusions and Recommendations

1. A pressurized tank sprayer was used successfully in pesticide applications on two turf test plots. Analysis of nine deposition coupons from each test yielded average deviations in deposition rate of 8.8% relative standard deviation (RSD) for a pesticide/fungicide application and 10.7% RSD for an acid herbicide application.

2. The turf plots used in this study were typical of local area lawns as opposed to professionally maintained test plots such as have been used in other studies of this type. As such, the turf density of these "real world" test plots was lower, and they contained a substantial proportion of weeds.

3. Laboratory and field quality control sample results showed no target analytes detected in sample media or in field blanks collected on untreated test plots. Field and laboratory spiked sample results indicated a problem with inefficient extraction of chlorothalonil, dicamba, mecoprop, and 2,4-D from PUF sleeves. Spike recoveries of the acid herbicides were also low for the denim cloth samples.

4. For all three dislodgeable residue collection methods, sample handling for turf samples was complicated by the adherence of grass clippings and debris to the sample media following sample runs. This problem was most severe for the PUF roller, which collected about 20 times more material, by weight, than either the California roller or the Dow sled.

5. Analysis of grass clipping and debris samples removed from PUF roller and California roller samples collected from the acid herbicide test plot revealed that target analyte levels in the grass clippings and debris samples were 50 times higher than levels in the PUF sleeves and 2–6 times higher than levels in the California roller cloths.

6. In the comparison of the PUF roller and Dow sled methods on turf treated with chlorpyrifos and chlorothalonil, neither method exhibited good sampling precision, with results ranging from 20 to 50% RSD. The Dow sled yielded better consistency in the transfer efficiency data, and neither method exhibited a clear trend as to the effect of sampling direction relative to the mower direction used.

7. In the comparison of the PUF roller and the California roller methods on turf treated with the acid herbicides, dicamba, mecoprop, and 2,4-D, the PUF roller sampling precision averaged near 45% RSD, while the California roller precision was a surprisingly good 12% RSD on average. Transfer efficiency was variable for the PUF roller averaging about 0.2%, while the California roller exhibited consistent transfer efficiency at about 0.5%. For the three sampling directions tested, sampling precision was lower for the PUF roller for sampling in the same direction as the mower and, for the California roller, precision was higher for sampling in the opposite direction.

8. The evaluation of the PUF roller method on treated turf revealed several inherent problems with the technique in this real-world application. Sampling precision was generally poor, pesticides were not efficiently extracted from the sample media, and the PUF media was inordinately prone to collecting grass clippings and debris during sample runs. For these reasons we do not recommend that the PUF roller method be used for dislodgeable residue sampling on turf.

9. The evaluation of the Dow sled method on treated turf was limited because of the instability of the 3- x 3-in. sled used. The available data show that sampling precision was low, but transfer efficiency was consistent. The denim cloth media does not tend to collect grass clippings and debris, but the low extraction efficiency for acid herbicides is a source of concern. Further evaluation of the Dow sled method on turf is recommended, but a larger sled base will be required.

10. The evaluation of the California roller method on treated turf yielded results showing high sampling precision and consistent transfer efficiency. The percale sheet sampling media does not tend to collect grass clippings and debris, and extraction efficiency of the acid herbicide target analytes was good. These results, along with the availability of a handle assembly permitting upright operation of the roller, form the basis for our giving the California roller method the best rating of the three methods evaluated in this study.

11. The results of tests comparing the levels of the target analytes found in grass clippings and debris removed from the sample media to the levels found in the media itself establish the extreme importance of scrupulous cleaning of the dislodgeable residue sampling media, either at the time of sampling, or at least prior to extraction for analysis.

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The complete report, entitled "Evaluation of Methods for Collecting Dislodgeable Pesticide Residues from Turf," (Order No. PB98-114390; Cost: $21.50, subject to change) will be available only from:
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